2008

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ELSEVIER

Journal of Archaeological Science 35 (2008) 912–921

Journal of Archaeological SCIENCE

http://www.elsevier.com/locate/jas

Development and evaluation of geochemical methods for the sourcing of archaeological maize

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Received 14 April 2007; received in revised form 22 June 2007; accepted 25 June 2007

Abstract

Strontium (Sr)-isotope values on bone from deer mice pairs from 12 field sites in the Chaco Canyon area, New Mexico, were compared with isotope values of synthetic soil waters from the same fields. The data indicate that mice obtain Sr from near-surface sources and that soil samples collected at depths ranging from 25 to 95 cm contain Sr that is more accessible to the deep roots of maize; thus, synthetic soil solutions provide better data for the sourcing of archaeological maize. However, the Sr-isotope composition of mice may be more valuable in sourcing archaeological remains of animals such as rabbit, turkey, and deer.

In a separate study, five Native American maize (*Zea mays L.* ssp. *mays*) accessions grown out at New Mexico State University Agricultural Science Center, Farmington, New Mexico were used to determine if soil-water metal pairs partition systematically into cobs and kernels. The sampled maize included landraces from three Native American groups (Acoma, Hopi, Zuni) that still occupy the Four Corners area. Two cobs each were picked from 10 plants of each landrace. Partitioning of the Ba/Mn, Ba/Sr, Ca/Sr, and K/Rb metal pairs from the soil water to the cob appears to behave in a systematic fashion. In addition, 51 rare earth element (REE) pairs also appear to systematically partition from the soil water into cobs; however, the ratios of the REE dissolved in the soil waters are relatively invariant; therefore, the distribution coefficients that describe the partitioning of REE from the soil water to the cob may not apply to archeological cobs grown under chemically heterogeneous conditions. Partitioning of Ba/Rb, Ba/Sr, Mg/P, and Mn/P metal pairs from the soil water to kernels also behaves in a systematic fashion. Given that modern Native American landraces were grown under optimal environmental conditions that may not have been duplicated by prehistoric Native Americans, the distribution coefficients obtained in this study should be used with caution.

Keywords: Maize; Sr isotopes; Trace metals; Mice

1. Introduction

In this paper, we evaluate two geochemical methods for sourcing archaeological materials of biologic origin. In previous studies, Benson et al. (2003, 2006a) used strontium (Sr) isotopes and trace-metal ratios to infer the locations of field sites in which archaeological maize found in Pueblo Bonito, Chaco Canyon, New Mexico, may have been grown.

In the Sr-isotope studies, Benson and his colleagues compared the $^{87}Sr/^{86}Sr$ ratios of archaeological cobs with the $^{87}Sr/^{86}Sr$ ratios of Sr dissolved in synthetic soil waters prepared by the acid-leaching of soil samples collected from possible agricultural field sites. In the trace-metal study, they used a limited number of archived soil and cob samples from experimental agricultural plots at Crow Canyon Archaeological Research Center, Cortez, Colorado, and the New Mexico State University (NMSU) Agricultural Science Center, Los Lunas,

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0305-4403/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jas.2007.06.018

New Mexico, to estimate distribution coefficients for some metal pairs.

A distribution coefficient describes the systematic partitioning of a metal pair from soil water into a solid phase, in this case, a cob. The distribution coefficients were used, together with the trace-metal chemistry of several archaeological cobs, to estimate metal ratios of soil waters in which the maize was rooted. The estimated soil-water metal ratios were then compared with metal ratios of synthetic soil waters from several potential field sites in the Four Corners area to infer the maize's provenance.

These two approaches have certain inherent weaknesses. In the case of the Sr-isotope study, only a few ''point'' samples were obtained from each potential field site; and, in the case of the trace-metal approach, the data on which the metal-ratio distribution coefficients were based are extremely limited in terms of available soil-cob sample pairs. In a recent study, Benson et al. (2006b) found that systematic fractionation of metal pairs did not appear to occur within tule (*Schoenoplectus* cf. *acutus*) or willow (*Salix exigua*). These facts indicate that the systematic fractionation of trace-metal pairs from soil water into the cob or other parts of the maize plant needs to be more thoroughly studied.

In this paper, we describe the development and evaluation of geochemical methods used to determine possible source areas of archaeological maize. We compare Sr-isotope ratios of common deer mice (*Peromyscus maniculatus*) with Sr-isotope ratios of soil point samples from 12 field sites in the Chaco Canyon area. The mice integrate Sr over much larger surface areas (240–3000 m^2) than discrete soil samples and, therefore, may provide a better estimate of the mean Sr-isotope composition of a field site. In addition, we develop accurate distribution coefficients for metal pairs, using multiple soil-cob sample pairs from five landraces and multiple soil-kernel sample pairs from two landraces of Native American maize grown at the NMSU Agricultural Science Center at Farmington, New Mexico (Adams et al., 2006). We then compare the values of the newly derived distribution coefficients with previous distribution coefficient estimates that were based on only a few soil-cob sample pairs.

1.1. Sr isotopes

A radiogenic isotope is one that was produced by the decay of a radionuclide, but which itself may or may not be radioactive. In the case of Sr, there are two isotopes of interest, ^{87}Sr and ^{86}Sr. ^{86}Sr is a stable isotope, whereas ^{87}Sr is a stable radiogenic isotope produced by the radioactive decay of ^{87}Rb with a half-life of 48.8 billion years. Thus the $^{87}Sr/^{86}Sr$ ratio of a rock and the soil derived from it is a function of the initial $^{87}Sr/^{86}Sr$ ratio of the rock, its age, and the amount of ^{87}Rb initially present in the rock. However, the rate of production of ^{87}Sr is so slow that the $^{87}Sr/^{86}Sr$ ratio can be considered invariant over archaeological timescales.

The isotopes of Sr are nearly identical in their physical and chemical properties; therefore, isotopic fractionation does not occur during chemical and physical transformations. In terms of Sr delivery to a plant, the soil water takes on the $^{87}Sr/^{86}Sr$ ratio of the soluble soil component which, in turn, is transferred unchanged to the plant.

There have been numerous archaeological applications of Sr isotopes during the past decade, most of which involve defining a person's or animal's origin or migration pattern (e.g., Hoppe et al., 1999; Beard and Johnson, 2000; Price et al., 2002; Montgomery et al., 2003). Sr isotopes have been used to demonstrate that some of the timbers used in the construction of Chacoan great houses were probably harvested in the Chuska and San Mateo mountains (English et al., 2001) and that several maize cobs found in Pueblo Bonito were grown in fields at the base of the Chuska slope or in fields bordering the Rio Chaco west of Chaco Canyon (Benson et al., 2003, 2006a).

1.2. Trace-metals

In using trace metals to determine the source of archaeological plant material, we seek to link the chemical composition of archaeological plants to the chemical compositions of living plants found in archaeological source areas, or alternatively, we seek to link the archaeological plants to their former soil substrates. The former procedure requires that the plant in question is today found in all possible archaeological source areas, which is not the situation for maize in the Four Corners area. Therefore, a direct link must be forged between the chemistry of the archaeological cob and the chemistry of the soil or soil water from which maize obtained its chemistry. Benson et al. (2003, 2006a) invoked the use of the trace-element distribution coefficient (K_D), a coefficient commonly used in low-temperature geochemistry (e.g., Pingitore and Eastman, 1984) to describe the fractionation of trace metals between liquid and solid phases. The distribution coefficient between soil water and the cob is defined by

$$K_D(C_{TE1}/C_{TE2})_{Soil\ Water} = (C_{TE1}/C_{TE2})_{Cob}$$

Where C_{TE1}/C_{TE2} = the concentration (μg element/g soil) ratio of trace metals 1 and 2.

The use of the distribution coefficient accounts for the bioavailability of chemical species (they are part of the soil-water solution), and the use of a metal ratio negates the effect of changes in soil-water concentration on the concentrations of individual dissolved trace metals. However, K_D is not constant for all metal ratios. Metal pairs that contain a trace nutrient that the plant prefers to incorporate or a trace metal that the plant prefers to exclude (e.g. lead) may exhibit widely varying K_D values. In addition to being plant-species dependent, the K_D value also depends on the set of environmental conditions under which the plant grew; e.g., moisture or nutrient stress. K_D values will tend to be constant for element pairs that have similar chemical properties if those properties are neither essential nor harmful to the plant. The use of an elemental ratio also allows us to work with synthetic soil solutions produced by leaching a soil with a weak acid (see Section 2).

2. Methods

2.1. Maize processing

For this study we sampled 5 of the 155 Native American maize landraces grown out at NMSU's Agricultural Science Center at Farmington, New Mexico, during the summer of 2005 (see Adams et al., 2006 for a description of the maize project). Two cobs each were picked from 10 plants of each of the five landraces. The sampled maize accessions include landraces from three Native American groups (Acoma, Hopi, Zuni) that still occupy the Four Corners area. These landraces were chosen in the hope that they are similar to those grown by pre-Columbian Native Americans that occupied parts of the Four Corners region between A.D. 850 and 1300.

Endosperm types and accession information for the five landraces are as follows: Field plot 3042 (Acoma yellow flint or pop), USDA Plant Introduction Station Accession Number 218141; Field plot 3068 (Hopi [Moencopi] blue flour), USDA Plant Introduction Station Accession Number 218175; Field plot 3089 (Zuni blue flour), collected by Deborah Muenchrath and reported in (Muenchrath et al., 2002); Field plot 3122 (Acoma orange flour), USDA Plant Introduction Station Accession Number 218167; Field plot 3131 (Acoma red flour), USDA Plant Introduction Station Accession Number 218168. Formal collecting data can be found at the U.S.D.A. Agricultural Research Service Germplasm Resources Information Network (GRIN) at http://www.ars-grin.gov/npgs/.

The NMSU Agricultural Science Center at Farmington, New Mexico, used center-pivot irrigation to apply 60 cm of growing season irrigation water in daily or every-other-day applications of 0.75–0.90 cm of water. Fertilizer was twice applied to the fields which could theoretically support a 180 bushel/acre production (K. Adams, personal communication, 2007).

Cordell et al. (2001) previously showed that the apical and basal ends of maize are chemically indistinguishable (19 elements); thus, it is not necessary to homogenize an entire maize cob in order to obtain a representative sample. For this study, the center 4 cm of each cob was removed using a titanium knife. The kernels and cupules were removed and discarded, and the remaining maize cob was cut into small pieces, homogenized, and freeze dried. A 0.9- to 4.2-gram subsample was transferred to a clean platinum crucible for dry ashing in a muffle furnace. Ashing was accomplished by ramping the temperature of the furnace in 50 °C increments every 30 min from a starting temperature of 100 °C to a final temperature of 450 °C at which temperature the sample was kept for 16 h. After cooling to room temperature, the sample was transferred to a small Teflon vessel to which 2 ml of deionized (DI) water, 0.5 ml of high-purity concentrated HNO_3, 1.5 ml of high-purity HCL, and 1 ml of (hydrofluoric) HF acid were added. This solution was then evaporated to dryness on a sand bath. The residue was dissolved in 2 ml of concentrated HNO_3 evaporated on a sand bath and the procedure repeated; then 10 ml of DI water and 1 ml of HNO_3 were added to the vessel which was gently heated on the sand bath to near dryness. The residue was then diluted with 100 ml of DI water in a volumetric flask. Prior to metals analysis, approximately 30 kernels each from the Hopi Blue and Zuni Blue cobs, both of the flour (endosperm) variety, were prepared in the same manner as the cobs.

2.2. Soil processing

Thirty-two soil samples were collected by hand auger from 12 field areas in Chaco Canyon (Fig. 1). At some locations, multiple (3) samples were collected at different depths; at other locations, samples were collected from several sites from either the surface or from a depth between 0 and 55 cm (Table 1). All Chaco soil samples were collected during previously published studies (Benson et al., 2003, 2006a).

Soils also were collected from the bases of five Native American maize landraces (10 plants from each of 5 landraces) grown at the NMSU Farmington, New Mexico, 2005 grow-out site. A 7.5-cm-diameter soil auger was used to obtain representative soil samples from both sides of maize stalks at depths centered at 35 and 70 cm. These two sample depths were chosen because they fall within the rooting depth of maize; e.g., some roots of the Krug variety of maize penetrate 1.8 m with more than 80% of the total root mass reaching 1.2 m (Kiesslebach, 1949). The four soil samples were integrated into a single Ziploc plastic bag.

In order to produce a synthetic soil water, soils in this and previous studies (Benson et al., 2003, 2006a) were air dried, homogenized, and a 5-gram subsample of each soil was leached for 48 hours (h) with constant agitation using 500 ml of 1-M acetic acid prepared from distillation-purified glacial-acetic acid. These samples were sequentially filtered through 0.4- and 0.1-micrometer (μm) pore-size membrane filters prior to analysis. Metals in the synthetic soil water primarily come from the leaching of calcium carbonate and from the exchange of hydrogen ions for metal ions in expandable clays.

2.3. Deer mice processing

The deer mouse, *Peromyscus maniculatus*, is an extremely common rodent found in the Chaco Canyon area. During a 2003–2004 mammal inventory at Chaco Culture National Historical Park, the deer mouse comprised nearly 20% of all captures (Geluso and Bogan, 2005; Bogan et al., 2007). Although a formal *P. maniculatus* population range study has not been conducted in Chaco, available small mammal literature suggests this species ranges over 240–3000 square meters (dependent upon the type of habitat) (Bunker, 2001 and references therein). *P. maniculatus* habitat generally consists of shrubby vegetation and contains decent cover and abundant seed sources. *Sarcobatus vermiculatus* (greasewood), *Atriplex canescens* (four-winged saltbrush), *Chrysothamnus nauseosus* (rabbitbrush), *Lycium pallidum* (wolfberry), and *Artemesia tridentata* (big sagebrush) are common shrubs and are excellent

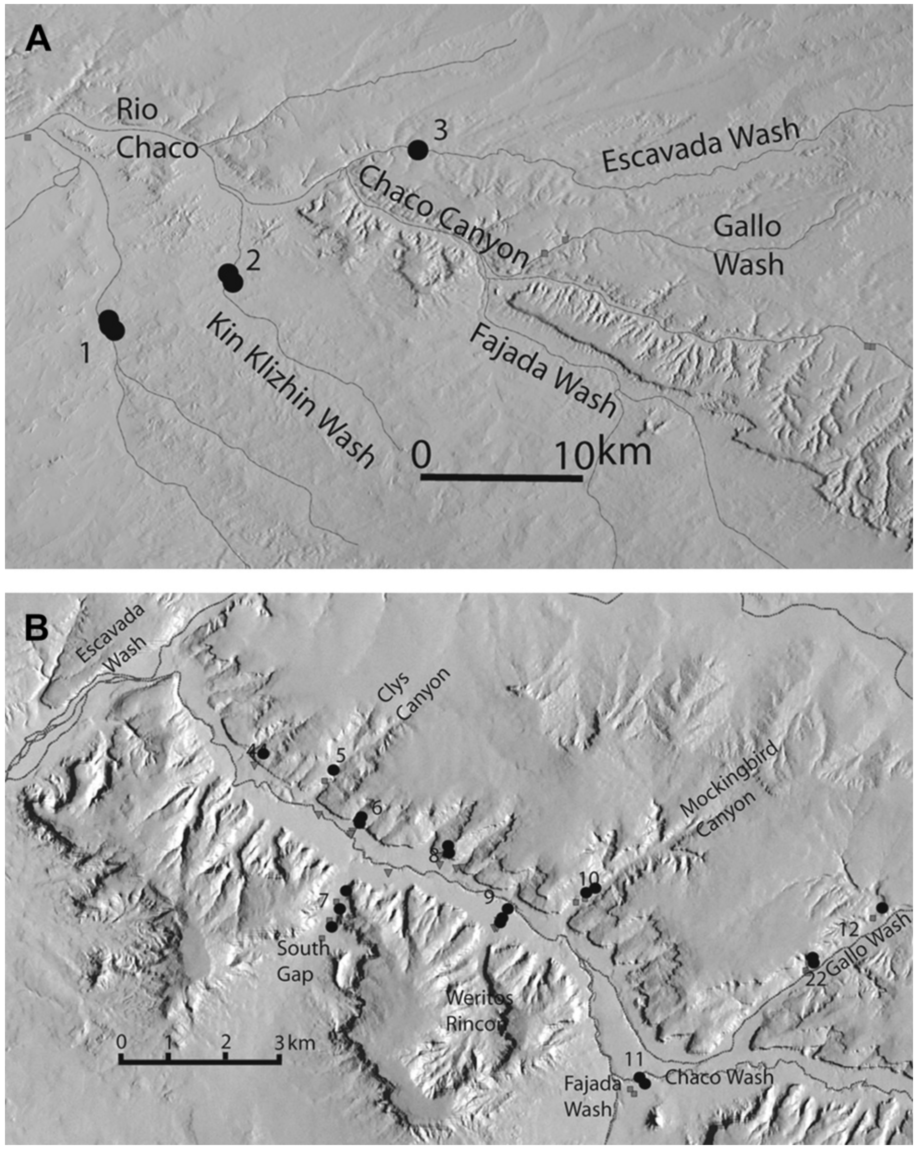

Fig. 1. Possible agricultural field sites within the Chaco Canyon area from which soil and deer mice were sampled. A. (1) Kin Bineola, (2) Kin Klizhin, (3) Escavada. B. (4) Penasco Blanco Field, (5) Clys Canyon, (6) Pueblo del Arroyo, (7) South Gap, (8) Chetro Ketl Field, (9) Weritos Rincon, (10) Mockingbird Canyon, (11) Fajada Butte, (12) Gallo Wash. North is at the top of each figure.

places to trap *P*. *maniculatus*. Deer mice subsist chiefly on seeds but they also consume fruits, bark, roots, and insects.

Rodents were collected at each of 12 sampling sites, including: Gallo Wash, Cly's Canyon, Chetro Ketl field, Penasco Blanco field, Weritos Rincon, Mockingbird Canyon, Fajada Butte, Pueblo del Arroyo, South Gap, Escavada Wash, Kin Klizhin, and Kin Bineola (Fig. 1). The latter two sites lie, respectively, 10 and 20 km southwest of the confluence of the Chaco and Escavada washes.

Rodents were trapped between January and May 2005 using collapsible live Sherman traps (HB Sherman Traps, Tallahassee, Florida), measuring $7.5 \times 9 \times 22$ cm. Each trapline was flagged and logged once using a Garmin GPSmap76 unit in datum NAD27. Pairs of Sherman live traps separated by 1–4 meters were placed at the base of shrubs in the evening. During the following morning, the traps were checked and two individuals of *P*. *maniculatus* were retained per site. The deer mice were quickly euthanized, individually bagged, and placed in a freezer in the lab.

Each of the 24 frozen specimens was processed in the following manner: the specimen was thawed and the skin, internal organs, and major muscle masses were manually removed with scissors and forceps. Specimens were then individually tagged using archival paper and air-dried for 24 h. Dried specimens were placed in a cardboard container in a dermestid beetle colony operated by the University of New Mexico Museum of Southwestern Biology's Mammal Division. After one week, all remaining muscle and connective tissue had been removed from the specimens by the dermestids. The specimens were then removed, placed in a plastic bag, and stored in a freezer for 7 days to kill any larva or adult dermestids. Prior to chemical analysis, the bones from each specimen were

Table 1
Site information and $^{87}Sr/^{86}Sr$ ratios for deer mice and synthetic soil solutions from sites within and near Chaco Canyon, New Mexico

Deer mouse Sr-isotope data								Soils Sr-isotope data							
Site No.	Site Name	Date Collected	Zone	UTM E	UTM N	$^{87}Sr/^{86}Sr$	2 Sigma	Site No.	Site Name	Depth (cm)	Zone	UTM E	UTM N	$^{87}Sr/^{86}Sr$	2 Sigma
CC05-1a	Cly's Canyon	06/01/2005	13S	232365	3995664	0.709634	0.000013	CC04-1	Clys Canyon	45–50	12S	772738	3995822	0.708792	0.000022
CC05-1b	Cly's Canyon	06/01/2005	13S	232365	3995664	0.709818	0.000011								
CKF05-1a	Chetro Ketl Field	15/01/2005	13S	234222	3994178	0.709209	0.000011	CK#1	Chetro Ketl Field	5–10	12S	774673	3994588	0.709190	0.000017
CKF05-1b	Chetro Ketl Field	15/01/2005	13S	234222	3994178	0.709262	0.000013	CKF#1	Chetro Ketl Field	25–35	12S	774683	3994453	0.709170	0.000012
								CKF#2	Chetro Ketl Field	55–65	12S	774683	3994453	0.709065	0.000015
								CKF#3	Chetro Ketl Field	85–95	12S	774683	3994453	0.709053	0.000009
EW05-1a	Escavada Wash	07/05/2005	13S	240779	3998290	0.709166	0.000014	EW04-1	Escavada Wash	45–50	12S	774001	3999476	0.709073	0.000028
EW05-1b	Escavada Wash	07/05/2005	13S	240779	3998290	0.709456	0.000011								
FB05-1a	Fajada Butte	04/04/2005	13S	237467	3990189	0.709125	0.000014	FB04-1	Fajada Butte	45–50	12S	778168	3990671	0.708973	0.000014
FB05-1b	Fajada Butte	04/04/2005	13S	237467	3990189	0.709243	0.000018	FB04-2	Fajada Butte	45–50	12S	778101	3990753	0.709005	0.000018
GW05-1a	Gallo Wash	05/01/2005	13S	241605	3993062	0.709312	0.000013	GW04-1	Gallo Wash	45–50	12S	782121	3993794	0.709311	0.000014
GW05-1b	Gallo Wash	05/01/2005	13S	241605	3993062	0.709621	0.000010	GW04-2	Gallo Wash	45–50	12S	781016	3992867	0.708963	0.000018
								GW04-3	Gallo Wash	45–50	12S	781056	3992821	0.708996	0.000012
KB05-1a	Kin Bineola	21/01/2005	12S	757669	3987748	0.709693	0.000014	KB04-1	Kin Bineola	45–50	12S	757669	3987748	0.709438	0.000013
KB05-1b	Kin Bineola	21/01/2005	12S	757669	3987748	0.709288	0.000006	KB04-2	Kin Bineola	45–50	12S	757663	3987602	0.709310	0.000012
								KB04-3	Kin Bineola	45–50	12S	757633	3987480	0.709324	0.000012
								KBV04-1	Kin Bineola Valley	50–55	12S	757222	3990342	0.709627	0.000020
KK05-1a	Kin Klizhin	07/05/2005	12S	764144	3990910	0.709678	0.000009	KK04-1	Kin Klizhin	45–50	12S	763797	3991159	0.709527	0.000011
KK05-1b	Kin Klizhin	07/05/2005	12S	764144	3990910	0.709545	0.000010	KK04-2	Kin Klizhin	45–50	12S	763995	3991388	0.709474	0.000016
MC05-1a	Mockingbird Canyon	19/01/2005	13S	236731	3993531	0.709529	0.000015	MC04-1	Mockingbird Canyon	45–50	12S	777227	3993962	0.709144	0.000013
MC05-1b	Mockingbird Canyon	19/01/2005	13S	236731	3993531	0.709707	0.000014	MC04-2	Mockingbird Canyon	45–50	12S	777075	3993897	0.709208	0.000019
PDA05-1a	Pueblo del Arroyo	04/04/2005	13S	232762	3994785	0.709232	0.000014	PDA#4	Pueblo del Arroyo	15–25	12S	773188	3994969	0.709093	0.000014
PDA05-1b	Pueblo del Arroyo	04/04/2005	13S	232762	3994785	0.709354	0.000020	PDA#5	Pueblo del Arroyo	0–3	12S	773158	3994925	0.709044	0.000017
S1005-1a	Peñasco Blanco Field	15/01/2005	13S	231128	3995963	0.709280	0.000011	S10#1	Penasco Blanco Field	25–35	12S	771485	3996044	0.709204	0.000015
S1005-1b	Peñasco Blanco Field	15/01/2005	13S	231128	3995963	0.709274	0.000007	S10#2	Penasco Blanco Field	55–65	12S	771485	3996044	0.709121	0.000017
								S10#3	Penasco Blanco Field	85–95	12S	771485	3996044	0.709078	0.000012
SG05-1a	South Gap	06/04/2005	13S	232375	3993103	0.709784	0.000013	SG04-1	South Gap	45–50	12S	772784	3993144	0.709421	0.000020
SG05-1b	South Gap	06/04/2005	13S	232375	3993103	0.709761	0.000012	SG04-2	South Gap	45–50	12S	772898	3993453	0.709617	0.000029
								SG04-3	South Gap	45–50	12S	773006	3993777	0.709709	0.000020
WR05-1a	Weritos Rincon	19/01/2005	13S	235100	3993101	0.709711	0.000014	WER#1	Weritos Rincon	25–35	12S	775694	3993419	0.709590	0.000010
WR05-1b	Weritos Rincon	19/01/2005	13S	235100	3993101	0.709742	0.000010	WER#2	Weritos Rincon	55–65	12S	775694	3993419	0.709606	0.000018
								WER#3	Weritos Rincon	85–95	12S	775694	3993419	0.709549	0.000001
								WR#1	Weritos Rincon	0–10	12S	775710	3993536	0.709570	0.000021
								WR#2	Weritos Rincon	0–10	12S	775651	3993412	0.709465	0.000008

UTM zone and coordinates are relative to NAD 27 datum.

dried, crushed, weighed, and dissolved in high-purity nitric acid, followed by dilution to the appropriate volume for the analytical method used.

2.4. Sr-isotope analyses

Strontium chemical separations and isotopic determinations were conducted in a Class 1–10,000 clean room at the University of Colorado, Boulder. Strontium separates were obtained using a Sr-specific resin (Sr resin SPS, Eichrom Technologies, Inc.). The total procedural blank for Sr was ~30 picogram (pg). Strontium isotopic measurements were obtained using a Finnigan-MAT 261 thermal-ionization mass spectrometer in 4-collector static mode. During the study period, 31 measurements of the SRM-987 Sr isotopic standard yielded a mean $^{87}Sr/^{86}Sr$ value of 0.71028 ± 0.00002 (2σ-mean) which is identical, within the precision of the measurement (two parts in the fifth decimal place), to the reference value of the standard (0.71028).

2.5. Trace-metal analyses

Multi-element trace-metal determinations were performed using inductively coupled plasma-mass spectrometric (ICP-MS and ICP-AES) methods (Garbarino and Taylor, 1993; Taylor, 2001). All measurements were made on aqueous sample solutions without preconcentration, using direct pneumatic nebulization with a Perkin-Elmer Elan 6000 instrument. ICP-MS and ICP-AES analyses were done for 51 trace elements for the maize cobs and kernels and 52 trace elements for the synthetic soil waters.

3. Results

3.1. Comparison of $^{87}Sr/^{86}Sr$ ratios of mice and synthetic soil waters

A comparison of deer mouse and soil-water $^{87}Sr/^{86}Sr$ ratios from the same field area (Table 1, Fig. 2) indicate that, at 11 of 12 fields in the Chaco Canyon area, the mice had higher $^{87}Sr/^{86}Sr$ ratios. Soil $^{87}Sr/^{86}Sr$ data as a function of depth are available for three fields (Chetro Ketl, Penasco Blanco, and Weritos Rincon). Two of the sites (Chetro Ketl and Penasco Blanco) exhibit decreasing $^{87}Sr/^{86}Sr$ ratios with depth with the uppermost soil water having nearly the same value as mice from the same field (Table 1). The single near-surface soil at Chetro Ketl field (CK#1) also has a $^{87}Sr/^{86}Sr$ value close to that of deer mice that occupied this field. These data suggest that the deer mice may be sampling plants and insects that obtain their Sr mostly from near-surface soils. If this is correct, then $^{87}Sr/^{86}Sr$ values from soils at somewhat greater depths are preferred for comparison to archaeological cob $^{87}Sr/^{86}Sr$ values because the root system of maize extends from the surface to about 1.5 m (Kiesslebach, 1949).

The Weritos Rincon field, whose near-surface soil-water $^{87}Sr/^{86}Sr$ values are substantially lower than the $^{87}Sr/^{86}Sr$ values of deer mice, is a somewhat unique environment in Chaco Canyon. Weritos Rincon soils, which are eolian in origin, experience semi-continuous reworking by wind and water, and many of the sampling sites are associated with surface drainage features (levees and flood channels) which formed in response to reworking of the soil. Therefore, the $^{87}Sr/^{86}Sr$ value of the soil surface in Weritos Rincon probably varies with time and space.

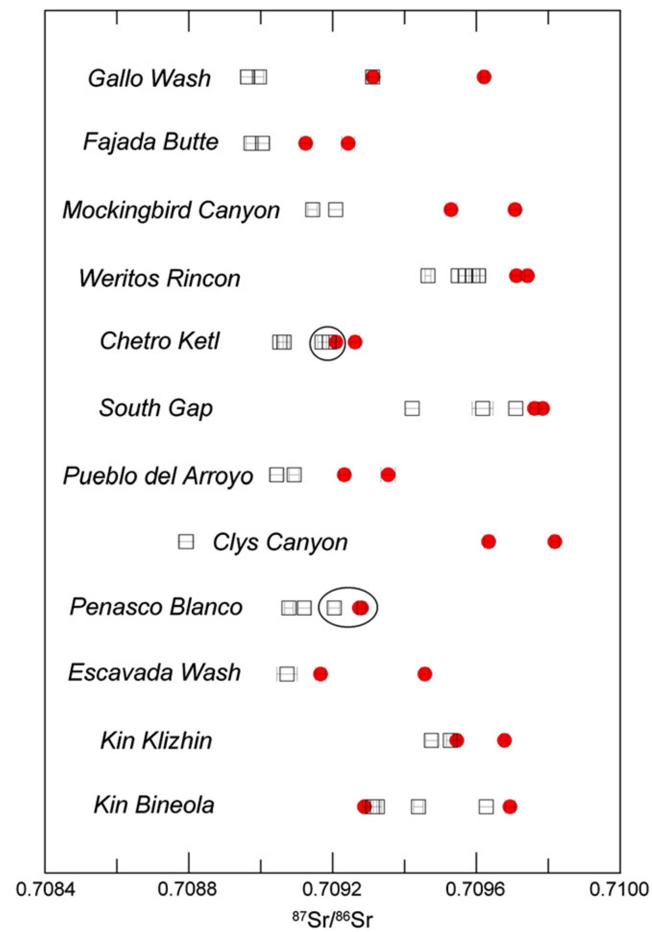

Fig. 2. Deer mouse and synthetic soil-water $^{87}Sr/^{86}Sr$ ratios for 12 field sites in the Chaco Canyon area. Solid circles indicate deer mouse samples. Open squares indicate soil samples. Ellipses enclose near-surface soil value and deer mouse $^{87}Sr/^{86}Sr$ values from the same field site that indicate mice are obtaining their Sr from near-surface biological sources.

3.2. Calculation of distribution coefficients for metal pairs

The metal data for Farmington maize cobs, kernels and synthetic soil waters are listed in Supplementary Tables 1–3. The cobs had 36 metals that were significantly above their detection limits; the kernels had 24, and the soil waters had 38. Using an EXCEL-based program, we calculated all possible metal ratio values for cobs, kernels, and soil waters. We then calculated K_Ds for soil-water:cob and soil-water:kernel metal pairs using five cob landraces and two kernel landraces. Using the criteria that the standard deviation of a metal pair K_D for a particular landrace had to be ≤33% of its mean value, we determined that four metal pairs (Ba/Mn, Ba/Sr, Ca/Sr, and K/Rb) exhibited systematic distribution coefficients between soil waters and cobs and that four metal pairs (Ba/Rb, Ba/Sr, Mg/P, and Mn/P) exhibited systematic distribution coefficients between soil waters and kernels for all landraces studied (Table 2).

Fifty-one REE metal pairs also partitioned systematically into the Farmington cobs; distribution coefficients of two of those pairs are listed in Table 2. Eu and Gd have about the same atomic number (63 and 64) and Y and Yb have the most disparate atomic numbers of the REE studied (39 and 70). Thus, we have chosen to illustrate the statistical values (mean and standard deviation) of distribution coefficients for REE pairs that exhibit minimally and maximally different chemical properties within the Lanthanide series that overall exhibits remarkably similar properties. Whereas, the REE pairs appear promising in terms of their systematic partitioning from the soil water to the cob; unfortunately, the soil-water pairs exhibited minimal variability at the NMSU Agricultural Science Center field site. For example, mean and 1-sigma values for $(Y/Yb)_{soil\ water}$ and $(Eu/Gd)_{soil\ water}$ for 100 samples are, respectively, 18.5 ± 1.2 and 0.232 ± 0.006. The lack of variability in the soil-water REE calibration data set renders indeterminate the applicability of the calculated REE K_Ds to archaeological maize.

It should be noted that one shortcoming of using deer mice $^{87}Sr/^{86}Sr$ as a proxy for biological available $^{87}Sr/^{86}Sr$ at a site is that the trace-metal composition in mice bone can not be related to the trace-metal composition of maize grown in the fields in which the mice foraged.

3.3. Comparison of newly calculated distribution coefficients with those used in previous studies

In previous studies involving archaeological cobs, three metal pairs (Ba/Sr, Mg/Sr, and Y/Yb) with roughly estimated K_Ds of, respectively, 0.30, 7.2, and 2.0 were applied. In this study we found that K_D (Ba/Sr) has a value of 0.24 ± 0.06, K_D (Mg/Sr) has a value of 7.5 ± 4.1, and K_D (Y/Yb) has a value of 0.75 ± 0.19. The large 1-sigma value of K_D Mg/Sr renders it undesirable as a tracer of provenance.

3.4. Illustration of the application Sr isotopes and newly calculated distribution coefficients to archaeological cobs

In Table 3 we have listed the calculated Ba/Sr ratios of synthetic soil waters for six cobs found in Pueblo Bonito (Benson et al., 2003) and compared them with measured Ba/Sr ratios of synthetic soil waters whose $^{87}Sr/^{86}Sr$ ratios fell within the range of Pueblo Bonito cob $^{87}Sr/^{86}Sr$ values (Fig. 3). Measured soil-water Ba/Sr ratios that match cob-calculated soil-water Ba/Sr ratios are shown in bold.

Three synthetic soil-water Ba/Sr ratios from the Rio Chaco system, two from Chaco, and one from the Chuska slope fall within the range of the calculated Pueblo Bonito cob soil-water ratios (Table 3, Fig. 3). This result is similar to that

Table 2
Distribution coefficient (K_D) values for six metal pairs in five cob landraces and for four metal pairs in two kernel landraces

Maize cob type	K_D (Ba/Mn)	1-s	K_D (Ba/Sr)	1-s	K_D (Ca/Sr)	1-s	K_D (K/Rb)	1-s	K_D (Eu/Gd)	1-s	K_D (Y/Yb)	1-s
Acoma yellow	0.067	0.021	0.285	0.058	0.121	0.030	4.00	1.11	1.26	0.38	0.84	0.31
Acoma orange	0.067	0.017	0.243	0.063	0.141	0.050	3.48	0.70	1.24	0.27	0.72	0.11
Acoma white	0.077	0.022	0.214	0.065	0.179	0.041	3.97	0.84	1.17	0.27	0.71	0.11
Hopi blue	0.069	0.029	0.217	0.036	0.144	0.031	5.21	0.97	1.31	0.31	0.67	0.13
Zuni blue	0.078	0.027	0.230	0.048	0.171	0.030	4.68	2.05	1.17	0.40	0.79	0.17
Mean and Variability	***0.072***	***0.024***	***0.24***	***0.06***	***0.15***	***0.04***	***4.27***	***1.35***	***1.23***	***0.33***	***0.75***	***0.19***
Maize kernel type	K_D (Ba/Rb)	1-s	K_D (Ba/Sr)	1-s	K_D (Mg/P)	1-s	K_D (Mn/P)	1-s				
Hopi blue	0.00025	0.0007	0.35	0.13	0.051	0.010	0.0071	0.0019				
Zuni blue	0.00017	0.0007	0.27	0.06	0.052	0.005	0.0065	0.0011				
Mean and Variability	***0.00021***	***0.0008***	***0.31***	***0.11***	***0.051***	***0.008***	***0.0068***	***0.0015***				

Mean K_D values and their 1-sigma values are shown in bold and were calculated using all the cob (100) and kernel (20) samples.

Table 3
Pueblo Bonito calculated cob soil-water Ba/Sr ratios compared with Ba/Sr ratios in synthetic soil solutions for samples whose $^{87}Sr/^{86}Sr$ ratios fall within the range of Pueblo Bonito cobs

Sample No.	Ba/Sr
Calculated soil-water Ba/Sr ratios for cobs found in Pueblo Bonito	
H-242/242A	0.82 ± 0.14
H-242/242B	1.41 ± 0.24
H-254/258A	0.74 ± 0.13
H-254/258B	0.68 ± 0.12
H-254/258C	1.05 ± 0.18
H-7673	0.56 ± 0.10
Rio Chaco soil-water Ba/Sr ratios	
CDR04-1	**1.56**
CDR04-3	**0.85**
ES04-2	0.17
GB04-2	0.40
KB04-1	0.40
KB04-2	0.36
KB04-3	0.45
KK04-2	**0.46**
PP04-3	2.21
PP04-5	2.44
Chaco side-canyon and valley-floor soil-water Ba/Sr ratios	
GW04-1	3.14
LH#2	**1.46**
MC04-2	1.77
SG04-1	**1.11**
WR#2	2.26
Chuska slope soil-water Ba/Sr ratios	
CT#1	0.11
CTW#1B	0.19
CTW#1C	0.11
CTW#2B	0.43
SS#1	**0.57**
SS#3	0.35
TGHBM#4	0.16
TGHBM#5	0.21
TGHBM#6	0.10

Values in bold indicate synthetic soil-water samples whose $^{87}Sr/^{86}Sr$ and Ba/Sr ratios match those associated with Pueblo Bonito cobs.

illustrated in Table 21-4 in Benson et al. (2006a) in which six synthetic soil-water Ba/Sr ratios from the Rio Chaco system, two from Chaco, and one from the Chuska slope fell within the range of calculated Pueblo Bonito cob:soil-water ratios. Thus our newly derived distribution coefficient for the Ba-Sr metal pair does not, in general, change our concept of where Pueblo Bonito maize may have been grown; however, our repudiation of the accuracy and applicability of the Mg-Sr and Y-Yb metal pairs weakens the argument that the Chuska slope may have been the principal source of several cobs found in Pueblo Bonito (Benson et al., 2003).

We urge caution with regard to the application of K_Ds derived in this study to archaeological cobs. The modern Native American maize grown in the study of Adams et al. (2006) was not grown under environmental conditions usually experienced by prehistoric southwestern Native Americans; i.e., the Farmington crop was raised using optimal irrigation and fertilization. It is possible that prehistoric southwestern Native Americans increased nutrient loadings by burning fields

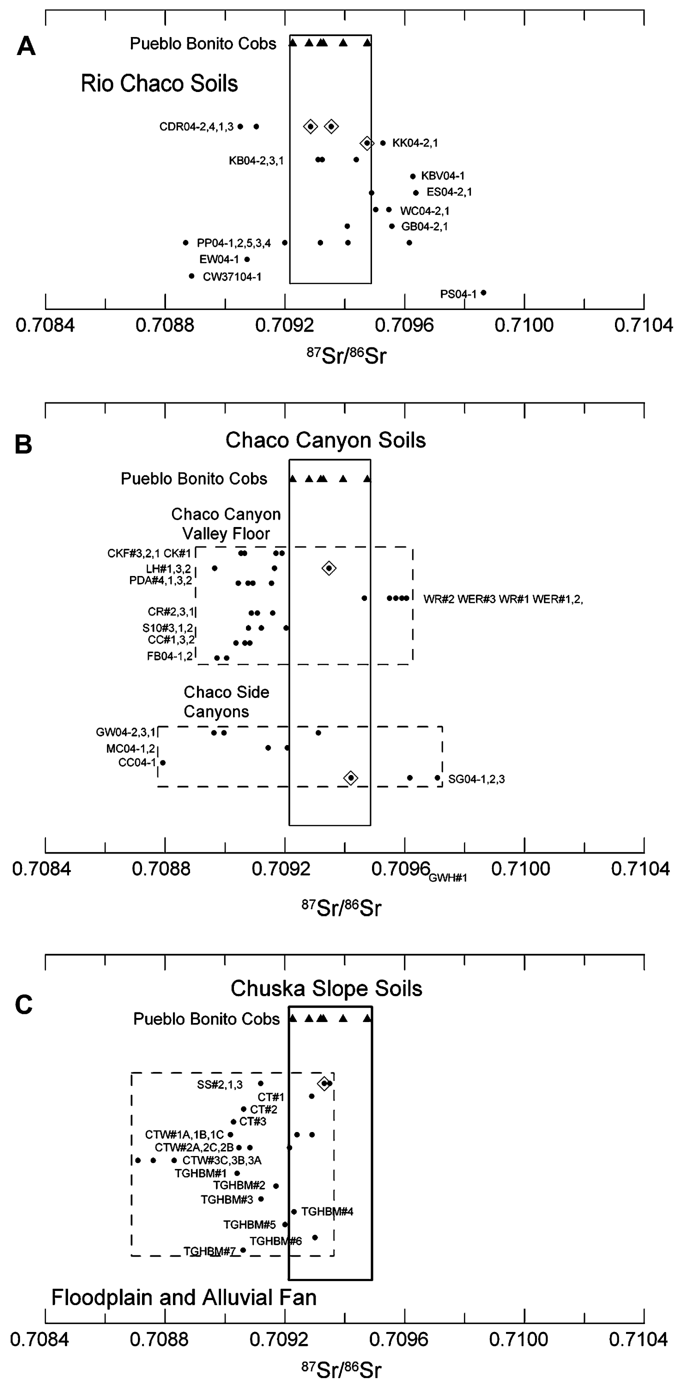

Fig. 3. Solid rectangle encloses soil water $^{87}Sr/^{86}Sr$ ratios that match Pueblo Bonito archaeological maize cobs; diamonds enclose soil waters whose Ba/Sr ratios match soil waters in which Pueblo Bonito maize cobs grew. **A**. Comparison of $^{87}Sr/^{86}Sr$ ratios of Pueblo Bonito archaeological cobs with $^{87}Sr/^{86}Sr$ ratios of synthetic soil solutions from floodplain and side tributary deposits along the Rio Chaco (see Fig. 21-3 in Benson et al. (2006a) for site names and locations). Previously unpublished data of L. Benson is shown for CDR04 (Casa del Rio): 1–4, PP04 (Pueblo Pintado): 3–5 and PS04-1 (Peach Spring). **B**. Comparison of $^{87}Sr/^{86}Sr$ ratios of Pueblo Bonito archaeological cobs with $^{87}Sr/^{86}Sr$ ratios of synthetic soil solutions from valley floor (floodplain) and side-canyon tributary deposits along the Rio Chaco within Chaco Canyon (see Fig. 21-2 in Benson et al. (2006a) for site names and locations.) **C**. Comparison of $^{87}Sr/^{86}Sr$ ratios of Pueblo Bonito archaeological cobs with $^{87}Sr/^{86}Sr$ ratios of synthetic soil solutions from floodplain and alluvial fan deposits in the Chuska slope (see Benson et al. (2006a) for site names).

(increasing phosphorous) and by the addition of urine (increasing nitrogen) (see Adams (2004) and references therein). However, these practices would not have completely mitigated the environmental stress experienced by the prehistoric maize plant. Such stress may have impacted the partitioning of metals into cobs and kernels. In addition, the amount of water applied to the Farmington maize during the growing season was four times the mean-annual historic precipitation received at 45 of 66 weather stations in the Four Corners region and twice the amount received at 64 of the stations during the historical period of record (Fig. 8 in Benson et al., 2007).

Most of the 155 cob types grown at the NMSU Agricultural Science Center averaged about 20 cm in length and 4 cm in diameter (kernels attached) (Appendix 2 in Adams et al., 2006). In contrast, the unburned archaeological cobs from Pueblo Bonito range in length from 5 to 10 cm and in diameter from 2 to 3 cm (kernels removed). This suggests that archaeological maize was grown under less-than-optimum conditions, and implies that environmental stress may have affected the fractionation of trace metals from the soil water into the cob. Thus, we put more confidence in the ability of $^{87}Sr/^{86}Sr$ to act as a tracer of archaeological maize than we do trace-metal pairs.

4. Conclusions

This study has demonstrated that deer mice in the Chaco Canyon area of northwestern New Mexico obtain their Sr from plants and insects that mostly sample the upper several centimeters of soil. Thus, the $^{87}Sr/^{86}Sr$ ratios of deer mice are more useful in the sourcing of organisms (e.g., deer and rabbit) that sample plants with shallow root systems than plants such as maize whose roots often extend to about 1.5 m.

Previous studies that attempted to evaluate the systematic partitioning of metal pairs into plants either failed to document such an occurrence (Benson et al., 2006b) or were based on very few data (Benson et al., 2003, 2006a). To confirm or deny the applicability of metal-pair distribution coefficients that describe such partitioning, we sampled cobs, kernels, and soils from five maize landraces grown at the Farmington NMSU Agricultural Science Center during the summer of 2005. The results of our study indicate that four metal pairs and numerous REE metal pairs exhibited systematic partitioning between soil water and cobs and also that four metal pairs exhibited systematic partitioning between soil water and kernels. Because the REE metal pairs exhibited only minimal variability in soil water from the NMSU Agricultural Science center site, we are not confident in the applicability of REE K_D values calculated from the NMSU-based data sets.

The value of cob and kernel K_Ds may not be strictly applicable to studies of archaeological maize given that the modern Native American landraces were grown under optimal conditions, which were infrequently, if ever, achieved during the cultivation of archaeological maize. Therefore, we suggest that until K_Ds are obtained for Native American maize landraces grown under conditions typical of that experienced by prehistoric plants that their present values be applied with caution.

At this time, the best tool for sourcing archaeological maize remains Sr isotopes. A substantial percentage of the samples from a potential field site should have cob-matching soil-water $^{87}Sr/^{86}Sr$ ratios in order to demonstrate that the field was the source of ancient maize. For example, only 4 of 36 synthetic soil-water samples in Chaco Canyon and no more than one soil water from any field has a $^{87}Sr/^{86}Sr$ ratio that falls within the range of archaeological cobs from Pueblo Bonito (Fig. 3B). This contrasts sharply with the Rio Chaco area in which 10 of 37 samples have $^{87}Sr/^{86}Sr$ ratios that fall within the range of archaeological cobs (Fig. 3A). Three Rio Chaco field areas have multiple samples with cob-matching soil-water $^{87}Sr/^{86}Sr$ ratios (3 out of 3 samples from the Kin Bineola field, 2 out of 5 samples from the Pueblo Pintado area, and 2 out of 4 samples from the Castle del Rio site) that indicate a high probability of those sites being a source of archaeological maize.

Acknowledgments

Any use of trade, product, or firm names in this paper is for descriptive purposes only and does not imply endorsement by the U.S. government. We thank the Navajo Nation Chaco Sites Protection Program for financial support of the analytical effort. Our appreciation also to Elizabeth Wolfe, Terry Plowman, David Roth, and Ron Antweiler who performed the laboratory studies and data reduction. Thanks also to Karen Adams who encouraged our efforts and provided access to the NMSU Agricultural Science Center study site and especially to Lindsay Werth who planted the maize. The $^{87}Sr/^{86}Sr$ analyses were performed at the University of Colorado by G. Lang Farmer, and D. Eberl created the EXCEL program that was integral to the calculation of K_Ds. We also thank two anonymous reviewers for their helpful comments.

Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jas.2007.06.018.

References

Adams, K.R., 2004. Anthropogenic ecology of the North American Southwest. In: Minnis, P.E. (Ed.), People and Plants in Ancient Western North America. Smithsonian Books, Washington, D.C., pp. 167–204.

Adams, K.R., Meegan, C.M., Ortman, S.G., Howell, R.E., Werth, L.C., Muenchrath, D.A., O'Neill, M.K., Gardner, C.A.C., 2006. MAIS (Maize of American Indigenous Societies) Southwest: ear descriptions and traits that distinguish 27 morphologically distinct groups of 123 historic USDA maize (*Zea mays* L. spp. *Mays*) accessions and data relevant to archaeological subsistence models. (http://spectre.nmsu.edu (Projects And Results, Collaborative MAIS Experiment).

Beard, B.L., Johnson, C.M., 2000. Strontium isotope composition of skeletal material can determine the birth place and geographic mobility of humans and animals. Journal of Forensic Sciences 45, 1049–1061.

Benson, L., Cordell, L., Vincent, K., Taylor, H., Stein, J., Farmer, G.L., Futa, K., 2003. Ancient maize from Chacoan great houses: where was it grown? Proceedings of the National Academy of Sciences 100, 12111−13115.

Benson, L., Stein, J., Taylor, H., Friedman, R., Windes, T.C., 2006a. The agricultural productivity of Chaco Canyon and the source(s) of pre-Hispanic maize found in Pueblo Bonito. In: Staller, J.E., Tykot, R.H., Benz, B.F. (Eds.), Histories of Maize: Multidisciplinary Approaches to the Prehistory, Biogeography, Domestication, and Evolution of Maize. Elsevier/Academic Press, Amsterdam, pp. 289−314.

Benson, L.V., Hattori, E.M., Taylor, H.E., Poulson, S.R., Jolie, E.A., 2006b. Isotope sourcing of prehistoric willow and tule textiles recovered from Great Basin rock shelters and caves − proof of concept. Journal of Archaeological Sciences 33, 1588−1599.

Benson, L., Petersen, K., Stein, J., 2007. Anasazi (pre-Columbian Native American) migrations during the middle-12th and late-13th centuries − were they drought induced? in: Diaz H. (Ed.), Climate and Cultural Change History in the Americas, Climatic Change DOI: 10.1007/s10584-006-9065-y.

Bogan, M.A., Geluso, K., Haymond, S., Valdez, E.W., 2007. Mammal inventories for eight national parks in the Southern Colorado Plateau Network: Aztec Ruins National Monument, Bandelier National Monument, Chaco Culture National Historical Park, El Malpaís National Monument, El Morro National Monument, Petroglyph National Monument, Salinas Pueblo Missions National Monument, and Yucca House National Monument. Natural Resource Technical Report NPS/IMR/SCPN/NRTR—2007/[001]. U.S. Department of the Interior, National Park Service, Natural Resource Program Center Fort Collins, Colorado.

Bunker, A., 2001. *Peromyscus maniculatus* (online), animal diversity web, http://animaldiversity.ummz.umich.edu/site/accounts/information/Peromyscus_maniculatus.html.

Cordell, L.S., Durand, S.R., Antweiler, R.C., Taylor, H.E., 2001. Toward linking maize chemistry to archaeological sites in the North American Southwest. Journal of Archaeological Science 28, 501−513.

English, N.B., Betancourt, J.L., Dean, J.S., Quade, J., 2001. Strontium isotopes reveal distant sources of architectural timber in Chaco Canyon, New Mexico. Proceedings of the National Academy of Sciences 98, 11891−11896.

Garbarino, J.R., Taylor, H.E., 1993. Inductively Coupled Plasma-Mass Spectrometric Method for the Determination of Dissolved Trace Elements in Natural Water. U.S. Geological Survey Open-File Report 94−358.

Geluso, K., Bogan, M.A., 2005. Mammalian Inventories for Three National Parks in the Southern Colorado Plateau Network, Bandelier National Monument, Chaco Culture National Historic Park, El Malpais National Monument. U.S. Geological Survey Final Report 2003−2004, 78 pp.

Hoppe, K.A., Koch, P.L., Carlson, R.W., Webb, S.D., 1999. Tracking mammoths and mastodons: reconstruction of migratory behavior using strontium isotopes. Geology 27, 439−442.

Kiesslebach, T.A., 1949. The Structure and Reproduction of Corn. In: University of Nebraska Agricultural Experiment Station Research Bulletin 161. University of Nebraska Press, Lincoln.

Montgomery, J., Evans, J.A., Neighbour, T., 2003. Sr Isotope evidence for population movement within the Hebridean Norse community of NW Scotland. Journal of the Geological Society, London 160, 649−653.

Muenchrath, D.A., Kuratomi, M., Sandor, J.A., Homburg, J.A., 2002. Observational study of maize production systems of Zuni farmers in semiarid New Mexico. Journal of Ethnobiology 22, 1−33.

Pingitore, N.E., Eastman, J.P., 1984. The experimental partitioning of Ba^{2+} into calcite. Chemical Geology 45, 113−120.

Price, T.D., Burton, J.H., Bentley, R.A., 2002. The characterization of biological available strontium isotope ratios for the study of prehistoric migration. Archaeometry 44, 117−135.

Taylor, H.E., 2001. Inductively Coupled Plasma-Mass Spectrometry: Practices And Techniques. Academic Press, San Diego.